CORROSION-RESISTANT PROTECTIVE OVERCOAT FOR MAGNETOOPTICAL MEDIA

T. K. Hatwar, S. C. Shin, and D. G. Stinson
Research Laboratories, Eastman Kodak Company,
Rochester, NY 14650

Abstract

Aluminum nitride thin films were prepared by RF reactive magnetron sputtering from an aluminum target in an Ar/N\textsubscript{2} atmosphere. The composition, structure, and the optical, chemical, and electrochemical properties of AlN films were investigated as a function of sputtering parameters. The ability of AlN overcoats to protect the magnetooptical (MO) TbFe layer was demonstrated by monitoring the Kerr hysteresis loop during an accelerated aging test. No significant change was observed in the MO properties for 30 days of aging at 70 °C and 30% relative humidity (RH). The results indicate that AlN is superior to SiO\textsubscript{2} as a protective overcoat. Electrochemical corrosion tests were carried out on AlN/TbFe films to examine the corrosion resistance provided by the AlN coating.

1. Introduction

Amorphous rare-earth/transition-metal (RE-TM) thin films are prominent candidates for high-density magnetooptical recording because of their low grain noise and perpendicular magnetic anisotropy [1]. However, these materials exhibit aging, which diminishes their MO characteristics. The changes in MO properties are attributed primarily to the selective oxidation of rare-earth metal atoms [2]. To improve the corrosion resistance of the RE-TM film, two general strategies have been adopted. One method is to improve the intrinsic corrosion resistance of the film by alloying elements like Al, Ti, Au, and Pt [3]. Improvements in corrosion resistance have been demonstrated by this method, but they are not sufficient to meet the requirements of a storage medium. Another method is to coat the film with a protective layer. This layer may also provide optical enhancement of the MO effect by altering the polarization-dependent reflectance of the overcoated film [4]. For this purpose, it is desirable for the overcoat to have a refractive index approxi-

mately equal to the square root of the index of the MO layer and good optical properties. Several types of materials such as metals, polymers, and ceramics can easily be deposited to form thin protective overcoat films on MO media. Metals have the inherent disadvantages of large thermal diffusivity and large absorption coefficients and high reflectivity. This reduces the sensitivity and linearity of the thermally driven recording process. Polymers have low thermal diffusivity, but may thermally degrade and have low mechanical strength at high temperatures. Also, polymers do not provide a hermetic oxygen and water vapor barrier. Ceramics are stable, have low thermal diffusivity, and provide a non-reactive surface. Coatings of SiO\textsubscript{2} are widely used as protective layers. However, it is well established that a SiO\textsubscript{2} antireflection coating does not provide sufficient protection to these media [2,5,6]. This suggests the use of a non-oxide overcoat with an appropriate refractive index, high optical transparency, high density, and good mechanical properties. We have studied aluminum nitride as a candidate protective overcoat and have found that it meets these criteria.

Aluminum nitride is a modern ceramic material. It has high thermal stability (decomposition temperature >2400 °C) and high resistivity. It has a high refractive index compared to glass and polycarbonate. It has been widely used in semiconductor devices as an insulating and passivating layer. Aluminum nitride was first used on MO media by Ohta, et al. [5]. The structure and morphology and, hence, the corrosion resistance of these films can be varied with the sputtering conditions. Here we present optical and chemical properties of aluminum nitride films under a variety of conditions. The aging characteristics of TbFe films protected with a SiO\textsubscript{2} or an aluminum nitride overcoat are discussed to demonstrate the corrosion protection offered by an aluminum nitride overlayer.

1.2. Film Preparation and Characterization

Aluminum nitride coatings were deposited by reactive magnetron sputtering of an aluminum target in an Ar+ N\textsubscript{2} atmosphere. The purity of the target was 99.9995%. The films were deposited on Si, glass, quartz, mica, and polycarbonate (PC) substrates. The substrate temperature was maintained below 98 °C to avoid thermal stress in the films. The substrate temperature is particularly important while depositing the protective films on TbFe films or PC disks. The difference in the thermal expansion coefficients of the insulating AlN film and the metallic TbFe film may give rise to high stress in the film which may affect its performance. Also, a slight increase in temperature may damage the PC substrate (T\textsubscript{g} = 150 °C) or alter the micron-sized pregroove morphology on the surface of the PC disk. The properties of the aluminum nitride films depend on the various sputtering parameters such as Ar:N\textsubscript{2} ratio, input RF power, total sputtering pressure, N\textsubscript{2} flow rate, and substrate temperature. The general conditions used were as follows: input RF power, 300-2000 Watts; Ar:N\textsubscript{2} ratio, 1:1; total gas pressure, 1-30 mTorr; N\textsubscript{2} flow rate, 3-5 sccm; substrate temperature, 68-98 °C; and target to substrate spacing, 50 mm.

Thin films of aluminum nitride between 20-1000 nm were prepared and evaluated for composition (Auger electron spectroscopy, infrared spectroscopy, ion scattering spectroscopy), structure (transmission electron microscopy, transmission electron diffraction and x-ray diffraction), optical transparency (UV-VIS-IR), refractive index (ellipsometry), and electrochemical corrosion.

The thin films of TbFe were prepared by coevaporation from electron beam heating of Fe and tantalum resistive boat heating of Tb. The coercivity and the Kerr rotation angle varied less than 5% across a 12 cm diameter sample. The composition of the films was determined by XRF. TbFe films with >15 at% of Tb showed the (110) x-ray diffraction peak of Fe, indicating that those samples had crystalline structures. However, samples with >15 at% of Tb revealed the amorphous phase. TEM and cross-sectional SEM studies showed that the amorphous film had a columnar structure, which consisted of high density regions 10 nm in diameter surrounded by a network of low density or void regions about 1 nm thick.

The Kerr hysteresis loops from bare and protectively coated TbFe samples were measured using a 635-nm HeNe laser. The thickness of TbFe films, 15-35 nm, exhibited uniaxial anisotropy normal to the film plane, as revealed by the existence of a perpendicular Kerr angle hysteresis loop. Within those compositions, the coercivity increased rapidly with Tb concentration until the room temperature compensation condition of 15 at% was reached. The composition dependence of the Kerr rotation angle, α, showed a similar, but much less pronounced behavior.
with the maximum Kerr rotation of \(2\theta_k = 0.4^\circ\) occurring at 22 at% Tb. The TbFe films used for AlN and SiO, overcoating had initial room temperature \(2\theta_k = 0.38^\circ\) and \(H_c = 3.5\) kOe.

2. Results and Discussion

In reactive sputtering of targets such as Al, the formation of aluminum nitride is considered to occur at the substrate, and not during transfer from target to substrate, or at the target. The input RF power density and sputtering pressure are important parameters controlling the deposition rate, the formation of aluminum nitride, and in turn the properties of the film. As shown in Fig. 1 (curve a), the deposition rate was proportional to the RF input power. This was true for a 1:1:1:1 \(\text{Ar:Al:N}_2\) mixture as well as other gas compositions. After the \(\text{Al}\) sputters from the target, the \(\text{Al-}\)Al reaction is expected to proceed more quickly than the \(\text{Al-}\)N\(_2\) reaction due to the dissociation step of the latter. A very high absolute sputtering rate of \(\text{Al}\) gives insufficient time for \(\text{N}_2\) dissociation, reaction with \(\text{Al}\), and formation of \(\text{AlN}\). This high \(\text{Al}\) sputtering rate leads to more \(\text{Al}\) inclusions in the \(\text{AlN}\) lattice. An X-ray diffraction pattern from an aluminum nitride film deposited at an input power density of 6.4 W/cm\(^2\), contains both \(\text{Al}\) and \(\text{AlN}\) peaks, indicating a mixed \(\text{Al-}\)AlN film. In contrast, the films deposited at low power density, 1.4 W/cm\(^2\), and low deposition rate of 5 nm/min contain about 20% oxide. This may be resulting from the reaction of sputtered aluminum with the residual oxygen. At low deposition rates, the \(\text{Al-}\text{O}\) reaction is much faster than the \(\text{Al-}\text{N}\) reaction.

At a given substrate temperature, the total sputtering pressure is also a critical parameter in determining the deposition rate. In Fig. 1 (curve b), the deposition rate is plotted as a function of total sputtering pressure, keeping the RF power constant at 1 kW. The deposition rate is maximum near the total pressure, 3-5 mTorr. The sputtering pressure is critical in determining the film morphology; low pressure produces smooth dense films, whereas, high Ar pressure gives a columnar, island-like structure.

RF sputter power and the sputtering pressure are found to control the optical properties of the films. In Fig. 2, the refractive indices of aluminum nitride films deposited on Si substrates are plotted as a function of RF power and sputtering pressure. The refractive index, \(n\) at \(\lambda = 633\) nm, increases as the power is increased, reaching a maximum value of 2.15. The extinction coefficient, \(k\) is almost negligible, \(-0.005\). In general, \(n\) decreased with increasing sputtering pressure, indicating that the density of the films is decreasing. RF sputter power and the sputtering gas pressure were optimized to give dense and corrosion-resistant stoichiometric films. The films deposited at 1 kW power and 3-5 mTorr sputter pressure and about \(-13\) nm/min deposition rates have the best optical, mechanical, and corrosion-resistant properties. The X-ray diffraction pattern indicates that these films are highly oriented with the c axis normal to the substrate surface. The crystalline size determined by TEM is 6-10 nm in a 60-nm thick film. Auger analysis of the film gives the concentration of \(\text{Al}\) and \(\text{N}\) as 10:50. The oxygen and carbon impurity contents are less than 3% each.

Spectral normal transmittance, \(T(\lambda)\) and near normal spectral reflectance were measured by double beam spectroscopy. Figure 3 shows \(T(\lambda)\) and \(R(\lambda)\) for a 100-nm thick AlN film on quartz. More than \(85\%\) transmission and \(15\%\) reflectance are observed over the visible region. The corresponding transmission of a fused quartz substrate alone is \(93\%\). Also, there is essentially no absorption in the film, \(T + R = 100\%\). It was also found that film deposited at 1 kW power level and 3 mTorr sputter pressure are non-dispersive and non-absorbing for 360 nm < \(\lambda < 900\) nm. These optical and mechanical properties of AlN films make them an excellent candidate for transparent protective coatings.
To evaluate the performance of AlN films as a protective overlayer, they were coated on TbFe MO layers on glass and PC substrates. Coercivity and Kerr rotation were measured as a function of time for both SiO₂ and AlN overcoated TbFe samples incubated at 70 °C and 30% RH. All the films had same coercivity, $H_c$ (3.5 kOe) before the aging. Drastic changes occurred as the annealing time elapsed. The relative performance of SiO₂ and AlN protective layers regarding changes in $H_c$ is shown in Fig. 4. In a high temperature environment, $H_c$ and $2\theta_K$ decrease monotonically with time for the SiO₂/TbFe films.

Perpendicular magnetization disappeared in SiO₂/TbFe films within four days of aging. Similar results were obtained on the bare TbFe films. The TbFe film protected with 80 nm of AlN showed almost no variation in $H_c$ or $2\theta_K$, even after 30 days. The results indicate that by using AlN as the protective layer, the variations in $H_c$ and $2\theta_K$ are greatly diminished.

To examine the corrosion resistance provided by the AlN coating, electrochemical corrosion tests were carried out on an unprotected TbFe film and an AlN coated TbFe film. The environment was a 0.1 M KCl/0.1 M chloroacetic buffer (pH = 3.1) solution, which is an aggressive oxidizing agent. The potentiodynamic polarization curves are shown in Fig. 5. The measured corrosion current for bare TbFe is 93.5 $\mu$A/cm² while that for AlN coated TbFe is 0.08 $\mu$A/cm². The corrosion current is proportional to the corrosion rate in electrochemical corrosion tests. The very low corrosion current for AlN/TbFe films as compared to pure TbFe indicates the high corrosion resistance afforded by AlN films.

**Fig. 3.** Spectral normal transmittance (T) and near normal reflectance (R) measured for an 100 nm aluminum nitride film on quartz substrate.

**Fig. 4.** Changes of coercivity $H_c$ as a function of aging time for TbFe films with SiO₂ and AlN overcoats.

**Fig. 5.** Potentiodynamic polarization curves of a) AlN/TbFe film and b) bare TbFe film in pH = 3.1 KCl/ chloroacetic buffer recorded at 1 mV/sec scan rate.

**Conclusions**

We have demonstrated that highly transparent, high refractive index films of AlN with good structural properties can be deposited on TbFe films by reactive RF magnetron sputtering. Considerably more corrosion protection is provided to a TbFe magneto-optical layer by AlN than SiO₂. The AlN layer also acts as an anti-reflective coating enhancing the Kerr rotation to more than eight times the original value. These properties make AlN a promising material for protection of MO media.

**References**


